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Amorphous $TM_{1-x}B_x$ alloy particles prepared by chemical reduction (invited)

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Amorphous transition-metal boron (TM-B) alloy particles can be prepared by chemical reduction of TM ions by borohydride in aqueous solutions. In the last few years systematic studies of the parameters which control the composition, and, in turn, many of the properties of the alloy particles, have been performed and are reviewed in the present paper. The most important preparation parameters which influence the composition are the concentration of the borohydride solution and the *p*H of the TM salt solution. By controlling these parameters it is possible to prepare amorphous alloy samples with boron contents from about 9 up to about 40 at. %.

I. INTRODUCTION

The most widely used technique for preparation of amorphous transition-metal (TM) boron alloys is the method of quenching a liquid sufficiently fast to a temperature below the glass transition temperature. Alloys produced by this liquid-quench technique[1,2] are commercially available and are, because of their soft magnetic properties, employed in, e.g., transformers,[2] as flux-gate sensors[3] and for magnetic shielding.

Cosputtering of the elements onto a substrate is another well-established method for preparing this type of alloys. It is a rather time-consuming method, but extremely useful for fundamental studies. Using this technique, one may prepare amorphous TM-B films with boron contents ranging between 10 and 90 at.%.[4,5]

There has been much interest in new methods for preparing amorphous TM-B alloys, and especially methods for preparing the alloys in the form of particles. Particles have the advantage that they may be compacted to any shape, they may be suspended in a liquid to make a ferrofluid, or they may be interesting for catalysis or magnetic recording applications. It is also of interest to study if the fundamental structural and intrinsic magnetic properties differ from those of ribbons and films prepared by the liquid-quench and sputtering techniques, respectively.[6–8]

Only a few methods are at present available for preparation of ultrafine amorphous TM-B alloy particles. Two methods make use of the sputtering techniques. Small amorphous particles in an Al_2O_3 matrix have been produced by cosputtering an amorphous ribbon and Al_2O_3.[9] Also, by cosputtering Fe and B onto a sputter-etched polymer substrate, fine amorphous Fe-B alloy particles can be produced.[10] Another method is to spark erode two electrodes in a dielectric fluid, where the electrodes are fabricated from the alloys of interest.[6]

In this paper we will be concerned with a chemical reduction method by which transition-metal ions are brought to the metallic state by reduction by the use of an alkali-metal borohydride in aqueous solution. Simultaneously, boron is incorporated and ultrafine amorphous TM-B alloy particles can thereby be produced. We will discuss some of the preparation parameters that have been found to influence the alloy composition, the size of the particles, the degree of crystallinity, and, in turn, the magnetic properties.

The use of borohydrides for preparing fine alloy particles dates back at least to the 1950's.[11] Oppegard, Darnell, and Miller[12] studied the magnetic properties, whereas Brown[13] studied the catalytic properties of particles prepared in ethanol. The particles were shown to contain boron, and Brown[13] suggested that the particles might be amorphous. The presence of the amorphous state was also suggested in later works[14,15] on the basis of x-ray diffraction studies. Recent Mössbauer,[7,8,16] x-ray-[16–18] and electron-diffraction,[8] extended x-ray-absorption fine-structure (EXAFS),[8] and annealing[8,16] studies have confirmed that amorphous transition-metal–boron-alloy particles, indeed, can be produced by reduction of transition-metal ions by borohydride. In Figs. 1 and 2 are shown the Mössbauer spectra and the Fourier-transformed EXAFS spectra, respectively, for $Fe_{62}B_{38}$ alloy particles prepared by the chemical reduction method. Spectra are shown for the particles as prepared and after heat treatment in an argon atmosphere at temperatures above the crystallization temperature. The broad absorption lines in the Mössbauer spectrum for the as-prepared particles reflect a distribution of hyperfine parameters and are indicative of the presence of an amorphous phase. The deduced magnetic hyperfine splitting is in good agreement with that of amorphous ribbons with a similar composition, prepared by the liquid-quench technique. The heat treatment results in phases with sharp absorption lines. The phases can be identified as α-Fe and Fe_2B.[8] The Fourier transform of the EXAFS data for the annealed sample shows a typical crystalline feature with the presence of several peaks, while the Fourier-transformed EXAFS spectrum for the as-prepared particles only reveals a single pronounced peak. This also indicates that the structure is amorphous. X-ray[8,16–18] and electron[8] diffractograms, similarly, show essentially one broad peak for the as-prepared sample.

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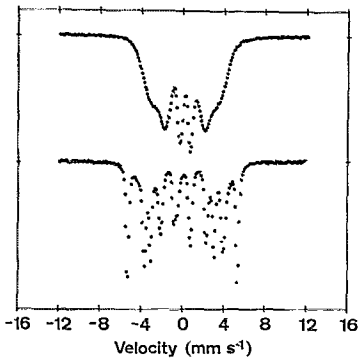

FIG. 1. Room-temperature Mössbauer spectra of as-prepared (upper spectrum) $Fe_{62}Ba_{38}$ particles and particles after annealing in an Ar atmosphere at 760 K for 5 h (lower spectrum). From Ref. 19.

In the past few years extensive work has been devoted to the studies of parameters that influence the composition of the particles, and some of these studies will be presented in the following.

II. PREPARATION METHODS

Three different ways of mixing the metal-salt and borohydride aqueous solution have been employed: (a) flows of the solutions react in a Y junction,[17] (b) the metal-salt solution is added dropwise to the borohydride solution,[16] or (c) vice versa.[7] The solutions may also be, e.g., based on ethanol,[13] and it has been found[20] that amorphous particles can be prepared using ethanol solutions. In this paper we will be concerned with mixing of aqueous solutions only.

The precipitate of particles is washed several times with distilled water and subsequently with acetone. The acetone-wet slurry is then dried for about 24 h in a flow of nitrogen or argon gas containing traces of oxygen. The oxygen produces a thin oxide layer on the particles which passivates them. Otherwise, the particles are pyrophoric in air. The samples are then characterized by chemical analyses to obtain their compositions. Sometimes part of the acetone-wet sample is frozen directly to liquid-nitrogen temperature in order to avoid the influence of the passivation layer on, e.g., the Mössbauer data.

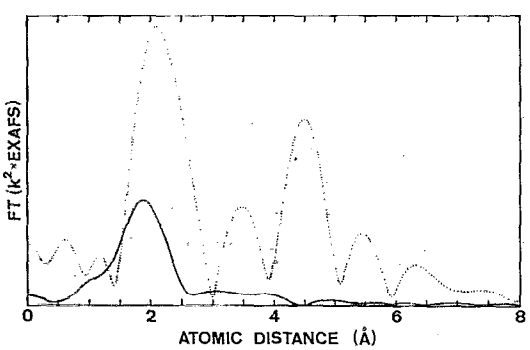

FIG. 2. Fourier-transformed EXAFS spectra of $Fe_{62}B_{38}$ alloy particles as prepared (solid curve) and after annealing in Ar (dotted curve) at 725 K for 4 h. From Ref. 8.

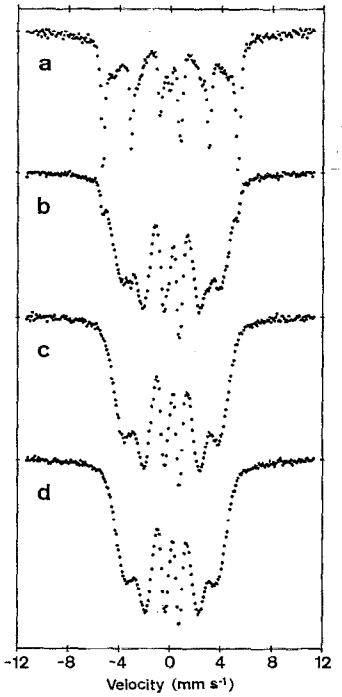

FIG. 3. Room-temperature Mössbauer spectra of Fe-B alloy particles prepared by dropwise addition to Fe^{2+} salt solutions of the following $NaBH_4$ solution concentrations: (a) 1, (b) 0.4, (c) 0.2, and (d) 0.1 mol. The samples were passivated in a flow of nitrogen gas containing about 100 ppm of oxygen. From Ref. 7.

III. DEPENDENCE ON BOROHYDRIDE CONCENTRATION

Using the Y junction, Yiping *et al.*[17] found the boron content in amorphous Co-B alloy particles to increase from 32 to 40 at. %, when increasing the borohydride concentration from 0.1 to 1.2 mol.

However, dropwise addition of an iron-salt solution to borohydride solutions with different molarities did not show any systematic variation, but resulted in amorphous Fe-B alloys with boron content in the 32–37-at. % range.[7]

On the other hand, dropwise addition of different concentrations of borohydride[7] to iron-salt solutions showed that the boron content of the particles depended on the borohydride concentration. In Fig. 3 are shown room-temperature Mössbauer spectra of Fe-B alloy particles prepared by adding 1-, 0.4-, 0.2-, and 0.1-mol $NaBH_4$ solution to 0.04-mol-solutions of $FeSO_4$. For the highest borohydride molarity, primarily α-Fe is produced. With decreasing borohydride molarity,the amount of this crystalline component decreases, and for molarities of 0.2 and 0.1 the Mössbauer spectra consist of a single sextet with broad absorption lines due to an amorphous Fe-B alloy, together with a small amount of a doublet due to Fe^{3+} in a thin passivation layer.

By varying the borohydride concentration, amorphous Fe-B alloy particles with boron contents between 28 and 33 at. % B have been produced.[7] Figure 4 shows the isomer shifts and magnetic hyperfine fields for such amorphous Fe-B alloy samples as a function of the boron content. In the same figure are also plotted data for samples prepared

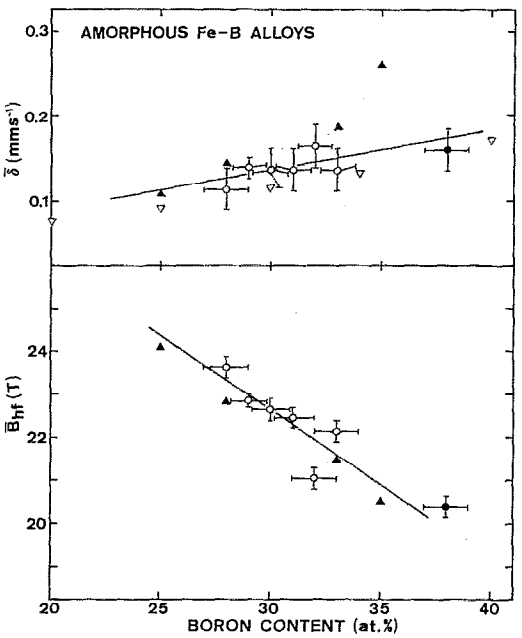

FIG. 4. Deduced average room-temperature magnetic hyperfine fields and isomer shifts vs boron content of amorphous Fe-B alloys prepared by the chemical reduction (Ref. 7) (open and solid circles), the melt -spinning (Ref. 21) (solid triangles), and the sputtering (Ref. 22) (open triangles) methods. The isomer shifts are given relative to α-Fe at room temperature. From Ref. 7.

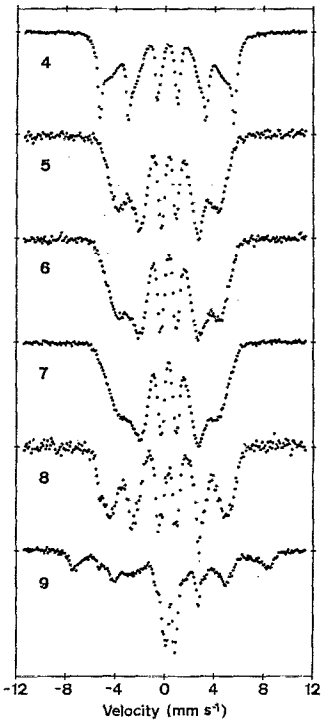

FIG. 5. Mössbauer spectra, obtained at 80 K, for samples prepared by dropwise addition of borohydride to an excess of Fe^{2+} ions with the *p*H of the Fe salt aqueous solution kept constant at the indicated values. From Ref. 23.

by the melt-spinning and the sputtering techniques. A good agreement between the data for amorphous ultrafine particles and bulk samples is evident. This seems in contrast to the conclusions of Berkowitz, Walter, and Wall[6] who reported that for $Fe_{75}Si_{15}B_{10}$ particles the saturation magnetization and Curie temperature decrease with decreasing particle size. The particles prepared by the chemical reduction method are considerably smaller (<200 nm) than those studied by Berkowitz and co-workers (>500 nm), and we still observe no significant differences of intrinsic properties between bulk and particle samples.

Dropwise addition of different concentrations of borohydride to Fe-Co salt solutions have, similarly, resulted in a variation of the boron content in the particles.[7] Amorphous $(Fe,Co)_{1-x}B_x$ alloy particles with x in the 18–28 at. % range have been prepared by this method. The Fe-to-Co ratio in the prepared particles was also found to depend on the borohydride concentrations.

It can be concluded that mixing similar solutions in different ways results in different compositions and dependencies on, e.g., the borohydride concentrations. The reasons for these differences should be found in other parameters that differ in the different mixing procedures. The initial *p*H of the borohydride and the metal-salt solution are about 9–10 and 3–4, respectively, and the *p*H during the reduction will be quite different if the transition- metal salt solution is added to the borohydride solution, or vice versa.

IV. DEPENDENCE ON *p*H

Recently,[23,24] it was discovered that through control of the *p*H of the transition-metal salt solution during addition of borohydride the composition of the particles may be altered significantly, even when the concentrations and addition times are kept the same. The boron contents of amorphous Fe-B alloy particles have by this technique been lowered down to about 15 at. % (Ref. 23). In the following we will discuss these results and also, in some detail, present new results.

The Fe-B alloy particles that are discussed below have been prepared by adding dropwise 200 ml of 0.1-mol $NaBH_4$ to 500 ml of 0.04-mol $FeSO_4$ over a period of approximately 1 h. The *p*H of the Fe salt solution was controlled during the reaction by simultaneous addition of 0.1-mol HCl or NaOH. Part of each sample was frozen to liquid-nitrogen temperature and studied by Mössbauer spectroscopy at this temperature. The Mössbauer measurements were obtained using a conventional constant acceleration spectrometer with a source of ^{57}Co in rhodium. The absorption lines were fitted to Lorentzian lines by a least-squares method.

Figure 5 shows the Mössbauer spectra for samples prepared with constant *p*H values of the Fe salt solution between 4 and 9. The *p*H was controlled to better than ± 0.5. A dramatic evolution with *p*H value is observed. For the lowest *p*H value, the spectrum reveals that the sample consists of both α-Fe and an amorphous alloy component. With increasing *p*H the samples become fully amorphous as seen by the absence of sharp lines due to crystalline components. At a *p*H of 8 ± 0.5, the magnetic hyperfine field is considerably larger than that for the samples prepared with the *p*H in the 5–7 range. This indicates that the

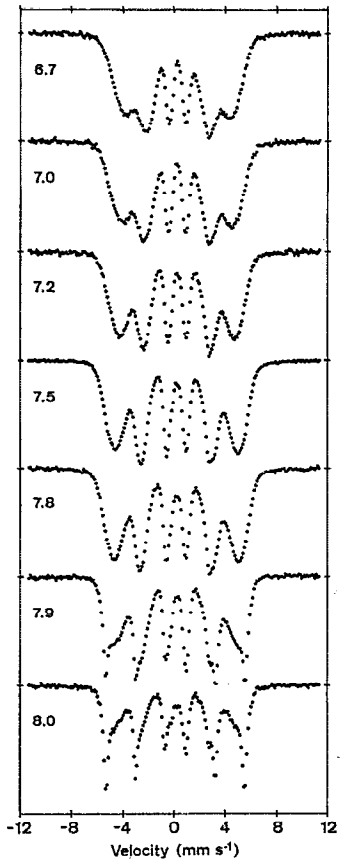

FIG. 6. Mössbauer spectra, obtained at 80 K, for Fe-B samples prepared with the Fe salt solution kept constant at the indicated pH values during the addition of borohydride. From Ref. 26.

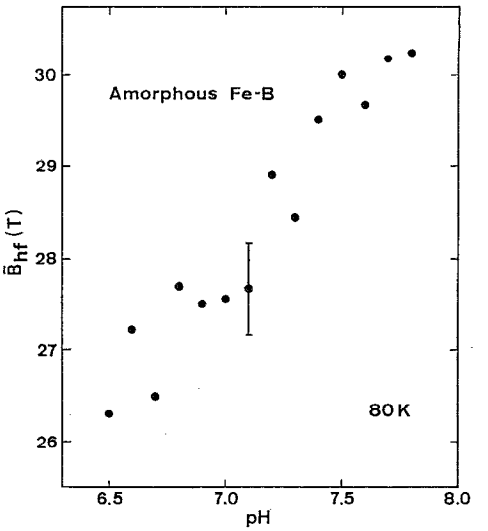

FIG. 7. The deduced average magnetic hyperfine fields for Fe in the amorphous Fe-B alloy particles as a function of pH.

boron content has decreased following high-pH preparation conditions. Indeed, chemical analysis yields a total boron content of about 12 at. % for a pH of 8, while about 28 at. % B is incorporated for the lower pH values.[23] A detailed analysis reveals that about 10% of the spectral area of the pH $= 8$ sample is due to α-Fe, suggesting the boron content in the amorphous Fe-B alloy to be about 14 at. %.[23] The deduced average hyperfine field is 28.4 ± 0.4 T and agrees well with the 28.9 ± 0.3 T found for amorphous $Fe_{85}B_{15}$ ribbons at 80 K.[25] Also,the linewidths were found to be similar.[23] The spectrum for the sample with pH $= 9$ shows that iron hydroxide is the main product at this pH.

The results presented in Fig. 5 suggested to us that a detailed study of the pH dependence between about 7 and 8 would be very interesting. Results of such studies[26] are discussed below.

In Fig. 6 are plotted Mössbauer spectra of samples prepared with pH values between 6.7 and 8.0. In this case the pH of the Fe salt solution was controlled with a pH-stat to better than 0.02. The spectra for pH $= 6.7$ and 7.0 resembles those of pH $= 6$ and 7, respectively, in Fig. 5. The magnetic hyperfine splitting is seen to increase gradually with increasing pH because of a decreasing boron content in the particles. Chemical analysis showed that the boron content in the particles prepared with pH equal to 7.8 was about 15 at. %, while it was about 28 at. % for the lowest pH values. For pH above 7.8, α-Fe appears in the spectra.

The magnetic hyperfine fields in the fully amorphous samples are shown versus pH in Fig. 7, and a nearly linear relationship between the magnetic hyperfine field and pH can be seen. The magnetic hyperfine fields for amorphous Fe-B alloy particles with boron contents of 15, 20, and 25 at. % are 30, 29, and 27.5 ± 0.5 T,[26] respectively. For ribbons with the same compositions, magnetic hyperfine fields of about 29, 27.5, and 27 T, respectively, have been reported[25]; hence, within uncertainties, a nice agreement is observed, though with a tendency for the magnetic hyperfine fields for the particles to be slightly larger than for ribbons. A nearly linear relationship between the isomer shift and boron content of the amorphous Fe-B alloy particles is also observed.[26] The isomer shift, given relative to α-Fe at room temperature, changes from about 0.16 to 0.22 mms^{-1} when the boron content increases from 15 to 25 at. %. These results are also in accord with those for ribbons. These results thus indicate that the intrinsic properties of amorphous Fe-B alloys do not differ for particle and bulk samples.

The influence of pH on the composition of amorphous Fe-Co-B[24] and Fe-Ni-B[27] alloy particles has also been investigated. In the case of Fe-Ni-B, the alloys were prepared by varying both the pH and the borohydride concentration. For borohydride concentrations above 0.2 mol, the Fe-Ni-B alloy particles were partly crystalline for all pH values, while at lower borohydride concentrations amorphous alloys could be prepared.[27] As for the Fe-B alloy particles, low pH values result in particles with some degree of crystallinity; for pH $= 8$ primarily Fe^{3+} and Fe^{2+} was observed, while for pH ranging between about 4 and 7 amorphous Fe-Ni-B alloy particles were formed. In Fig. 8 the Mössbauer spectrum for such an amorphous Fe-Ni-B alloy is shown. The overall composition of the sample is $(Fe_{45}Ni_{55})_{91}B_9$; i.e., an amorphous TM-B alloy sample with an extremely low boron content has been prepared. The magnetic hyperfine field is about 29 T,[27] which is sig-

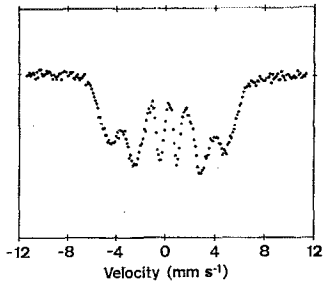

FIG. 8. Mössbauer spectrum for an $(Fe_{45}N_{55})_{91}B_9$ alloy obtained at 80 K. From Ref. 27.

nificantly higher than the about 27 T value[28] found for an amorphous $(Fe_{45}Ni_{55})_{80}B_{20}$ ribbon prepared by the liquid-quench technique.

V. ON THE VARIATION OF PARTICLE SIZE

In the previous chapters we have primarily dealt with control of the composition of the alloy particles. The size of the particles is also of outmost importance for their physical properties, e.g., their magnetic properties.

Oppegard and co-workers[12] found that the mean particle size of Fe-Co particles decreased by increasing the Co-to-Fe ratio in the aqueous metal-salt solution to which the borohydride was added. Uehori *et al.*[14] observed the same behavior. They found that the coercivity of Fe-Co alloy particles reached a maximum of about 1250 Oe for particles sizes of about 30 nm, which has been suggested to be the critical size above which particles are multidomain.[14] Employing a variant of the Y-junction method for mixing the solutions, Kim and Brock[29] found, besides the dependence on the Co/Fe and Ni/Fe ratios, that the particle size for particles prepared from a ferrous solution decreased with increasing reactor temperature. It is not certain that the particles prepared by these groups were amorphous, but if the interest primarily lies in preparing particles with high coercivities this question is of less importance. Yiping *et al.*[17] found, using a Y junction, that the particle size for amorphous Co-B alloys decreased with an increase of the borohydride molarity.

The decrease of the particle size with increasing Co/Fe and Ni/Fe ratios, borohydride molarities, and preparation temperatures may be explained by increased reaction rates. A higher reaction rate results in a higher production rate of metal atoms available for nucleation, which, in turn, may result in smaller particles. The results also indicate that Ni and Co ions react faster with the borohydride than do Fe ions. This also explains why the Co/Fe and Ni/Fe ratios in the particles often are enhanced with respect to the ratios in the solutions from which they are prepared.[7,29]

VI. ON THE STABILITY OF THE AMORPHOUS PARTICLES

The stability of the ultrafine amorphous particles is of interest when considering engineering applications. Of fundamental interest is the study of crystallization temperatures for comparison with those of bulk samples. For ribbons obtained by the liquid-quench technique, crystallization has been found to initiate at the surface of

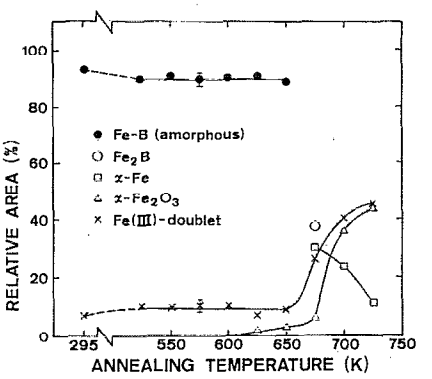

FIG. 9. The relative Mössbauer spectral areas for different iron-containing phases, as a function of annealing temperature in air, for $Fe_{62}B_{38}$ alloy particles. From Ref. 8.

the ribbons,[30] and one could therefore expect the particles to crystallize at lower temperatures than bulk samples. This seems, however, not to be the case. Thermomagnetization measurements in He on passivated, amorphous $Fe_{62}B_{28}$ particles[8] showed that the particles crystallize at 715 ± 10 K, which is close to the 735-K crystallization temperature found for films[31] with the same composition.

These particles were also found to be rather stable when heat treated in air. In Fig. 9 are shown the relative areas of different Fe-containing phases as deduced from Mössbauer spectra of amorphous $Fe_{62}B_{38}$ particles annealed 4 h in air in steps up to 725 K. The amorphous phase is seen to constitute 90% of the spectral area up to an annealing temperature of 650 K. Some α-Fe_2O_3 appears at 625 K and dominates together with an Fe^{3+} doublet after annealing at 700 K.

If passivated particles are kept at ambient temperature, we have not observed their structure to change. Baltz *et al.*[32] observed the saturation magnetization to decrease by about 30% when iron particles (not necessarily amorphous), prepared by the reduction with a borohydride, were stored in 80% relative humidity for 4 months. However, by chromating the particles by addition of potassium dichromate to the freshly prepared slurry, these authors found that the magnetization only slightly deteriorated over this period of time; i.e., the particles were stabilized by chromium at their surfaces.

VII. SUMMARY

The production of amorphous TM-B alloy particles by chemical reduction of TM ions by borohydride is by now a rather well-established technique. The verification of the amorphous structures has been given by results from x-ray- and electron-diffraction, EXAFS, and Mössbauer spectroscopies, and also crystallization studies have confirmed that amorphous particles indeed are formed.

Ultrafine $TM_{1-x}B_x$ alloy particles with x ranging between 9 and 40 at. % have been produced, a composition range that is larger than that obtainable by the melt-spinning method.

The influence of different preparation parameters on the composition of the alloy particles has been investigated in some detail, especially have systematic studies of the influence of the borohydride concentration and *p*H of the TM salt solution been performed, and both have been found to be of great importance. Parameters like temperature and addition rates are presumably of like importance, but have so far not been systematically investigated.

ACKNOWLEDGMENTS

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